Reply to "Comment on 'Charge order in Fe2OBO3: An LSDA+U study'"

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The experimental difficulties of observing Fe^{2+}/Fe^{3+} charge order in Fe_2OBO_3 and Fe_3O_4 are different and are considered separately. Charge order in Fe_3O_4 has a complex arrangement but is long-range coherent, as evidenced by a recent structure determination and two resonant x-ray diffraction studies. Long-range charge order has not been observed crystallographically in Fe_2OBO_3, although there is substantial indirect evidence for Fe^{2+}/Fe^{3+} ordering over shorter distances. Further support is provided by LSDA+U calculations on a doubled unit cell of Fe_2OBO_3, which shows a charge separation similar to that in Fe_3O_4, with a large t_{2g} subshell occupancy difference that is partially screened by Fe-O covalency.

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I. INTRODUCTION

The Comment by Garcia and Subias seeks to link our recent electronic structure calculations on Fe_2OBO_3 (Ref. 1) with selected resonant diffraction studies of Fe_3O_4, thereby disproving charge order (CO) in both materials. This connection is misleading, as the structural complexities that make it difficult to observe Fe^{2+}/Fe^{3+} charge order in the two materials are distinct. The two materials are described in the sections below, followed by a response to the criticisms of the computational study of Fe_2OBO_3.[1]

Compelling experimental evidence for CO comes from crystallographic studies of charge ordered superstructures in which expanded and contracted MO_n polyhedra are observed. Charge differences can be estimated from metal-to-oxygen distances, and the structural coordinates are also a necessary input for resonant x-ray diffraction analyses and electronic structure calculations that can corroborate the CO. Before considering the complex Fe_2OBO_3 and Fe_3O_4 structures, it is important to note that Fe^{2+}/Fe^{3+} charge order below a Verwey-type transition has been demonstrated in a simple perovskite system, $TbBaFe_2O_5$ (Ref. 2), and similar charge orderings (often accompanied by orbital ordering) are observed in many other transition metal oxides.[3] The charge separations, estimated from metal-oxygen distances around the crystallographically distinct transition metal sites, are consistently found to be reduced from the ideal values, for example, the estimated charge separation in $TbBaFe_2O_5$ is only 38% of the ideal Fe^{2+}/Fe^{3+} difference.[2] This generic feature of charge ordered oxides challenges the sensitivity of other experimental methods such as resonant scattering.

II. CHARGE ORDER IN Fe_3O_4

Charge ordering was first postulated to account for the 122 K resistive and structural Verwey transition in the spinel magnetite, Fe_3O_4. Despite investigations over more than 60 years, the full structure of the low temperature Verwey phase remains undetermined because of its complexity and its tendency to form twin domains. The monoclinic superstructure is known to contain 16 inequivalent octahedral "B" sites, over which Fe^{2+}/Fe^{3+} order is proposed to occur, in addition to eight inequivalent "A" sites for tetrahedral Fe^{3+}. Recent ^{57}Fe NMR experiments have confirmed these site multiplicities.[4,5] Although large, high quality, single crystals of Fe_3O_4 are available, these tend to microtwin when cooled below the Verwey transition, which frustrates attempts to determine the superstructure displacements by conventional single crystal diffraction experiments. The two published structure determinations, from a detwinned single crystal[6] and from a combined x-ray and neutron powder diffraction experiment,[7,8] have both reported the atomic displacements in a subcell equivalent to a quarter of the full monoclinic cell, in which the 16 B sites are averaged to four unique positions. Analysis of the recently determined structure,[8] showed a significant difference between mean Fe-O distances around the four averaged B sites corresponding to 20% of the ideal separation expected for Fe^{2+}/Fe^{3+} order. Each site is averaging over $(3Fe^{2+}+1Fe^{3+})$ or $(1Fe^{2+}+3Fe^{3+})$ sites, as confirmed by a subsequent resonant x-ray study,[9] and so the derived 40% of the ideal Fe^{2+}/Fe^{3+} charge separation is the same as is observed in $TbBaFe_2O_5$.

A complete determination of the anomalous x-ray scattering tensors at the 16 B sites of the Verwey phase would give insights into the charge ordering, and the orbital ordering expected for Fe^{2+} states, but such resonant diffraction experiments are technically very demanding given the above crystallographic difficulties. Scalar values of the anomalous dispersion terms are sensitive to charge states, and this has recently been used to verify the above charge ordering scheme in a resonant powder diffraction study.[9] The most detailed resonant single crystal x-ray study to date[10] has analyzed the energy variation of 50 Bragg reflections at the Fe K edge, confirming the 20% charge separation in the subcell of Refs 7 and 8, and providing some indications of the CO arrangement in the full supercell. Previous reports,[11] in

TABLE I. Comparison between total and l-projected charges and magnetic moments for inequivalent Fe atoms in the low temperature phases of Fe_3O_4 (from Ref. 15) and Fe_2OBO_3 (recalculated using a Fe radius of 2.125 au.).

Fe ion	Sample	q	q_s	q_p	q_d	q_d (Fe^{3+}/Fe^{2+})	M (μ_B)	M (Fe^{3+}/Fe^{2+}) (μ_B)
$Fe(B1)^{2+}$	Fe_3O_4	6.04	0.17	0.19	5.69	6	3.50	4
$Fe(B4)^{2+}$	Fe_3O_4	6.03	0.16	0.18	5.69	6	3.48	4
$Fe(1)^{2+}$	Fe_2OBO_3	6.21	0.18	0.22	5.81	6	−3.68	−4
$Fe(2)^{2+}$	Fe_2OBO_3	6.20	0.18	0.22	5.79	6	3.69	4
$Fe(B2)^{3+}$	Fe_3O_4	5.73	0.19	0.21	5.44	5	3.94	5
$Fe(B3)^{3+}$	Fe_3O_4	5.91	0.19	0.21	5.51	5	3.81	5
$Fe(1)^{3+}$	Fe_2OBO_3	5.98	0.21	0.24	5.53	5	−4.20	−5
$Fe(2)^{3+}$	Fe_2OBO_3	5.97	0.21	0.24	5.52	5	4.23	5

which CO was not observed, used more limited data sets of <10 reflections.

III. CHARGE ORDER IN Fe_2OBO_3

This material has a very different crystal structure to magnetite, with a substantial one-dimensional character. It is difficult to prepare and no single crystals have been grown to our knowledge. Previous experimental studies on polycrystalline samples found substantial indirect evidence for CO,[12–14] but the superstructure expected for full three-dimensional CO was not observed and so no superstructure model with distinct Fe^{2+}/Fe^{3+} sites was reported. This is very probably due to the 1-*d* nature of the underlying structure; the previous measurements suggest that Fe^{2+}/Fe^{3+} CO occurs within chains that make up quadruple ladders, but the CO is not long-range structurally coherent. Figure 4 of Ref. 13 shows that the direction of the monoclinic distortion is preserved through defects such as antiphase boundaries at which the CO is reversed, so that the long-range monoclinic distortion is not inconsistent with CO over much shorter length scales. However, any magnetic superstructure reflections arising from Fe^{2+}/Fe^{3+} CO will be broadened to the same degree as the (unobserved) CO superstructure scattering.

IV. ELECTRONIC STRUCTURE CALCULATIONS

The electronic structure calculations presented in Ref. 1 have enabled us to explore further whether CO is plausible in the postulated (but as yet unobserved) supercell of Fe_2OBO_3. The results show that the basic cell is unstable with respect to a doubled CO superstructure. By doubling the chain-axis periodicity, the calculation allows (but does not force) the two Fe sites in each chain to have inequivalent charge densities, although their structural environments are the same, and a charge difference corresponding to Fe^{2+}/Fe^{3+} CO is found for reasonable values of the Coulomb repulsion U.

The calculations result in two stable CO arrangements realized in the $2a\times b\times c$ $P2_1/c$ supercell. The first one is an antiferromagnetic CO solution presented in the paper. Besides, we also found a ferrimagnetic CO insulating solution with a charge separation between Fe1 and Fe2 sites (similar to Mn_2OBO_3) with spin magnetic moment of 1 μ_B per f.u. which contradicts to the experimental data.

Both solutions are almost degenerate, with the total energy of the antiferromagnetic solution being $\sim$0.01 eV/f.u. lower. However, this total energy comparison can hardly be considered as a decisive argument in favour of the antiferromagnetic solution since the calculations were performed neglecting possible oxygen displacements around differently charged Fe sites, whereas a larger value of the energy gain can be probably obtained due to the lattice distortion. Therefore, further calculations taking into account the lattice relaxation are of great interest.

Reference 1 thus adds further weight to the view that CO occurs in Fe_2OBO_3, at least over some short length scale. The result is achieved without introducing different oxygen displacements around the two Fe sites in the calculations, however, we do not propose that no such displacements occur. Strong electron-lattice coupling is found in all charge ordered transition metal oxides,[3] and CO in Fe_2OBO_3 will be accompanied by distortions over the same length scale, although these were averaged out in the previous structural analyses of the basic unit cell.

The quantitative comparison of calculated charges and moments for Fe_3O_4 (Ref. 15) and Fe_2OBO_3 (Ref. 1) in Table I of Garcia and Subias is invalid because the charges in the two studies were calculated within Fe spheres of different radii (2.125 and 2.5 au for Fe_3O_4 and Fe_2OBO_3, respectively). The choice of different radii was to decrease the number of empty spheres needed to fill the interatomic space, and to decrease the dimension of the Hamiltonian, in the respective calculations. To facilitate comparison, we have repeated the LSDA+U calculations for Fe_2OBO_3 using a Fe radius of 2.125 au (Table I). The results are not qualitatively different to those in Ref. 1, however, the Fe_2OBO_3 populations are now similar to those for Fe_3O_4. The *d*-electron populations (q_d) and magnetic moments in Table I show a bimodal distribution despite the different limitations of the structural models and the different degrees of spin frustration in the two systems.

Our criteria for assigning valence states to the Fe sites are based on similar calculations for single valent materials.

Analysis of the occupation matrices published for FeO (Ref. 16) showed one minority spin electron localized on a t_{2g} orbital with an occupation number of ~0.9, and the same criterion is used to identify Fe^{2+} in our study. For example, the majority Fe(1) states in Fe_2OBO_3 are occupied (all >0.9), whereas only one of the minority spin (t_{2g}) states of $Fe(1)^{2+}$ shows a substantial occupation number (0.91). In the identified Fe^{3+} ions, all minority spin states have small occupances (<0.3), in agreement with results from integer valent d^5 systems. This consideration shows that the states correspond to those of Fe^{2+} and Fe^{3+} in simple oxides, although the resulting charge separation is small. The minority spin Fe^{3+} states are partially occupied due to the formation of relatively strong σ-bonds with O $2p$ states, and this may account for the recent observation of charge modulations in O K edge spectra.[17] This so-called "static screening" phenomenon considerably decreases the total $3d$ charge separation between Fe^{2+} and Fe^{3+} cations.

LDA+U calculations for other mixed-valent transition metal oxides such as Ti_4O_7 (Ref. 18) have also found charge disproportionation between different cation sites. Although the separation is found to be small in all of these systems, the charge difference between t_{2g} subshells is always found to be large. This shows that the charge ordering scenario is valid although the strong covalent character of the transition metal to oxygen bonds distorts the charge distribution from a purely ionic distribution.

V. CONCLUSIONS

Translational-symmetry breaking transitions below which charge states order are found in a range of transition metal oxides, including Fe^{2+}/Fe^{3+} order in $TbBaFe_2O_5$, although the observed magnitude of the charge separation is consistently less than expected from an ideal ionic model. The charge and orbital ordering arrangement in Fe_3O_4 is complex and remains to be fully determined, but substantial progress has been made in the last five years, with direct crystallographic observation of Fe^{2+}/Fe^{3+} order in a subcell, despite partial averaging of sites, corroborated by electronic structure calculations and the most extensive resonant x-ray diffraction experiments.

Long-range CO has not been observed crystallographically in Fe_2OBO_3, although there is substantial indirect evidence for Fe^{2+}/Fe^{3+} ordering over shorter distances. The ground state calculated by the LSDA+U method for a doubled unit cell, in which Fe sites have the freedom to adopt different charge states, shows a charge separation similar to that in Fe_3O_4 and other oxides, with a large t_{2g} subshell occupancy difference that is partially screened by Fe-O covalency.

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